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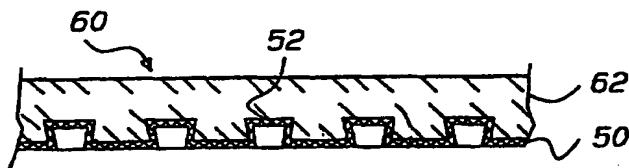
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(54) Title: IMPROVED SLAB OF RESIN-BOUND AGGLOMERATE MATERIALS AND RELATED MANUFACTURING PROCESS



intrusions that are closed at their end facing the mixture; c) transfer of the mixture, enclosed between a sheet or tray and a cover, to a press where it is de-aerated and pressed under vacuum in order to obtain the manufactured product in a raw state; d) application of heat to said raw product, while it still is enclosed between the above mentioned sheet or tray and cover, through a pair of heating planes in order to harden the binding resin.

(57) Abstract: Composite product formed by a slab consisting of an agglomerate of granular and filamentous inorganic materials bound with the use of structural resins which is coupled to a foil of thermoplastic material, and manufactured with a process comprising the steps of: a) preparation of a mixture capable of releasing air, i.e. adapted to be de-aerated; b) association to the mixture of a foil of thermoplastic material having hollow pro-

**IMPROVED SLAB OF RESIN-BOUND AGGLOMERATE MATERIALS AND
RELATED MANUFACTURING PROCESS.**

5

DESCRIPTION

The present invention refers to composite products that are formed by slabs of an agglomerate of granular, powder and possibly filamentous materials that are bound by means of resins. The invention also refers to the related manufacturing process.

Generally known in the art is a process for manufacturing slabs formed by granular inorganic materials bound with the use of an organic binder, comprising the steps of:

- (a) preparing a mixture made essentially of granular inorganic materials and an organic binder;
- 20 (b) pouring the mixture onto a support;
- (c) submitting the mixture to vibratory compaction under vacuum conditions, in which the mixture is pressed and vibrated in an ambient at a lower pressure than the atmospheric one;
- 25 (d) heating the compacted mixture to a temperature of catalysis of the organic binder so as to obtain the finished slab.

The above cited process and the related products represent a technique which, generally known under the name of "BRETONSTONE", was born a few decades ago and has in the meanwhile succeeded in breaking through both in Italy and abroad. As far as this particular technique is concerned, reference should be made to the Italian patents no. 912160 filed on 25th

September 1970 and no. 1056388 filed on 5th September 1975, both in the name of Marcello Toncelli.

This technique has since then been further developed, as at first the utilization was foreseen of two paper sheets to enclose the mixture to be submitted to vibratory compaction (Italian patent no. 1.117.346 filed on 22nd April 1977 in the name of Marcello Toncelli), and subsequently further improved through the introduction of considerable advancements, such as according to the Italian patent no. 1.288.566 filed on 29th January 1996, again in the name of the above cited assignee, where, instead of the sheets of paper, the use of two elements that enclose the slab is foreseen, wherein said elements are made of a material featuring a great elasticity, such as for instance rubber, the contact surface of which is treated so as to be made compatible with the mixture to be enclosed therein.

This technique has actually proven not only very effective and reliable, but also, and above all, quite flexible, and represents an important, primary development in the manufacture of slabs of agglomerate, as it is on the other hand confirmed by the diffusion all over the world of manufacturing plants based on the BRETONSTONE technology, which are used to make products of an excellent quality that are largely employed in a multiplicity of uses and applications.

In particular, a specific product that nowadays meets an increasingly higher demand on the market consists of large-sized slabs or panels that in the various workshops distributed all over the territory are cut to length and trimmed in a variety of manners so as to obtain therefrom elements for the building industry and/or the furniture making industry, such as inner and outer linings and facings, surfaces of tables and cabinets in general, kitchen worktops, vanity tops for bathrooms, door and window sills, door and window side-posts, staircase steps and floorings.

It is appropriate for the slabs to be of a large size (e.g. 310x135 cm), so as to be suitably cut according to the most varied requirements, as dictated by the particular plans, design options and laying systems.

5

So largely sized slabs must necessarily be manufactured to a suitable thickness in order to be able to withstand the various stresses that they are likely to undergo during their specific use, such as the impacts that may be imparted during their handling. It should in fact be born in mind that, in order to be able to reach the final user, the finished product must be packaged, stored, transported, cut to length and trimmed in situ. During all these handling and process phases, to prevent breakdowns or damages from occurring, a certain care and attention have to be applied that ultimately weigh considerably on the costs.

15

It should be noticed that BRETONSTONE products anyway have a greater physical-mechanical strength than any other natural stone material (the flexural strength may even amount to more than twice the highest values of natural stone materials), so that, for a given size, they may have a sensibly reduced thickness.

20

As a result, the agglomerate obtained with the above cited technique has found an affluent and flourishing outlet, as this has already been told earlier in this description.

25

On the other hand, the market diffusion of these products could be further increased to a quite considerable extent if the possibility were given to address also the very large market segment with a lower purchasing power. For such an aim to be reached, it is however necessary to reduce of a remarkable entity the manufacturing costs.

30

The end cost of the product depends on a number of factors, such as:

- the amount of raw material used (e.g. granular materials, sands, powders, resin, dyes and ancillaries);
- 5 - the weight of the product, which affects manufacturing and transport operations;
- the scraps deriving from the surface processing operations involving material removal;
- 10 - the thickness that heavily affects the cut-to-length operation carried out for the final laying down as it requires expensive tools and longer machining times.
- 15 It therefore is a purpose of the present invention to provide a product, along with the related manufacturing Process, which is effective in eliminating the above mentioned barriers that affect the existing technique; more specifically to provide a product which is again made in the shape of a slab of a considerably large size, but is at the same time
- 20 capable of being manufactured also to an extremely reduced thickness.

According to the present invention, this aim is reached in a manufacturing Process of the initially indicated kind, in which the slab of agglomerate is coupled to a foil of thermoplastic material, thereby bringing

25 about a composite product that actually preserves all of the advantageous characteristics of the BRETONSTONE product, has an extremely reduced thickness, and, like the traditional product, is really valuable under all aspects, from the aesthetical one to the physical-mechanical strength qualities, including abrasion resistance, resistance to staining, frost-proof

30 property and negligible water absorption capacity, chemical inertness when the used fillers are based on either quartz or other siliceous materials, wherein all such properties remain unaltered in the long run.

Furthermore, the already excellent impact strength properties of the traditional product are considerably boosted and this again is instrumental in enabling plates to be made having very large sizes and an extremely reduced thickness. In fact, coupling the slab of agglomerate
5 with a foil of thermoplastic material enhances to a noticeable extent the mechanical properties of the product, in particular the impact strength thereof. The reduction in thickness leads in turn to an appreciable reduction in the raw material costs of the new product.

10 Obviously, thanks to the thereby obtained general reduction in weight, also transport and handling costs are at the same time reduced. As far as the cost of the thermoplastic foil is concerned, this is more than compensated for by the saving effect generated by a corresponding reduction in the thickness of the agglomerate material; in addition, the
15 application of the thermoplastic foil on to the laying surface of the plate removes the operation of mechanical smoothing of the same surface, thereby reducing both tool and energy consumption significantly.

In particular, the thermoplastic foil used in the application is provided
20 with a number of protrusions that are intended to be embedded in the mixture, wherein said protrusions are hollow internally, closed on their side facing the mixture and open on the opposite side.

The cavities of the outwardly open protrusions on the laying face of the
25 slab enable the laying operation itself to be carried out with any material whatsoever, be it either a cement-based material, for instance a mortar, or any one of the several widespread glue materials existing on the market, which penetrate the cavities of said protrusions and get in this way firmly anchored in the foil.

30

The joining of the foil of thermoplastic material to the mixture of agglomerate is a perfect one, since the thermoplastic material of the foil

and the binding resin used in the mixture link up intimately with each other, being promoted by the thermal catalysis process. The protrusions that penetrate from the foil into the body of the slab constitute an additional mechanical link-up between the two elements.

5

According to a possible embodiment of the present invention, the surface of the foil of thermoplastic material which faces the mixture, and which therefore joins therewith, is previously roughened, although such a roughening effect may derive spontaneously from the manufacturing
10 process. In fact, during the vibratory compaction of the mixture, the granules that are present in the mixture cause the surface of the foil to undergo a slight abrasion and thereby bring about a roughening effect that further enhances the adhesion of the mixture to the same foil.

15 Again during the above cited phase of vibratory compaction, the protrusions of the thermoplastic foil undergo a slight deformation at their closed end portions, so that a kind of undercuts are created inside their cavities which are effective in preventing the mortar or the glue used for the bonding from coming out of the cavities inside which it is setting.

20

In the hot-hardening phase of the slab, which takes place at temperatures ranging from 100°C to 140°C, there first occurs a softening of the foil of thermoplastic material and, immediately thereafter, a hardening of the slab of agglomerate. Under such operating conditions,
25 the agglomerate slab is therefore able to shrink in an even and plain manner, since it is free of the constraining effect that the thermoplastic foil would certainly exert in its rigid (i.e. not softened) state.

When the agglomerate slab becomes eventually hardened and rigid, it
30 will have taken its final size, which is then maintained while cooling down. On the contrary, during the cooling down phase, the thermoplastic foil stiffens and retains the same plain dimensions which the slab had taken

in the hardening phase.

It should also be noticed that, during the heating up phase, a close link is created between the mutually contacting surfaces of the agglomerate
5 and the thermoplastic foil.

It is anyway important to stress the fact that the composite manufactured product according to the present invention actually supplements the existing BRETONSTONE agglomerate slab products for
10 targeting different market segments or, in other words, different kinds of customers/users, among which the very important "do-it-yourself" segment. In fact, slabs which are actually so thin, notwithstanding the really considerable dimensions thereof, can be handled and processed even by non-skilled personnel, as no professional tools or equipment are
15 actually needed for the said slabs to be cut and trimmed to length, but simple portable tools can be used instead. The composite manufactured products according to the present invention are well suitable for applications like lining furniture elements, such as tables, walls, and even for completely changing a floor covering without first removing the existing
20 one as it suffices to covering the latter with tiles that are light, easy to handle and practically unbreakable, being obtained from slabs having a very thin thickness.

The new product therefore further extends the inherently considerable
25 possibilities offered by the products manufactured according to the BRETONSTONE technique.

The features and advantages of the present invention will anyway be more readily and clearly understood from the following description that is
30 given by way of a non-limiting example with reference to the accompanying drawings, where :

- Figure 1 is a cross-sectional side view of a traditional plant used to manufacture slabs by vibratory compaction under vacuum conditions;

- Figure 2 is a perspective, partially cross-sectional view of the composite manufactured product obtained with the manufacturing Process according to the present invention;

- Figure 3 is a cross-sectional view of the composite manufactured product illustrated in Figure 2;

10

- Figure 4 is an enlarged-scale view of a detail of Figure 3;

- Figure 5 is a perspective view of the thermoplastic foil;

15 - Figure 6 is a cross-sectional view of a first variant of the thermoplastic foil;

- Figure 7 is a cross-sectional view of a second variant of the thermoplastic foil;

20

- Figure 8 is a view of a first embodiment of the composite product manufactured according to the present invention, in which the foil is embedded in the agglomerate slab;

25 - Figure 9 is a view of a second embodiment of the composite product manufactured according to the present invention, in which the slab is coupled to a double thermoplastic foil.

Figure 1 illustrates a prior-art plant used to manufacture slabs by means through vibratory compaction under vacuum conditions, which is built around a conveyor belt 10 moving forward in the direction shown by the arrow 12 and winding round the rollers 14 and 16, of which at least

one is motor-driven. The plant essentially comprises:

- (1) a first station A, where a bottom sheet or tray of rubber 20 is laid down;
- 5 (2) a second station B, where a film-forming agent (acting as a protecting barrier for the rubber underneath and as a release agent) is sprayed through nozzles 24 on to the underlying sheet 20;
- 10 (3) a third station G, where the mixture 26, which is carried along by the conveyor belt 28, is prepared;
- (4) a fourth station C, where the mixture is poured onto the underlying sheet 20, thereby forming a layer of material 30;
- 15 (5) a fifth station D, in which the mixture 30 is covered with an upper sheet or cover of rubber 32, on which the same film-forming agent has been sprayed in advance;
- 20 (6) a sixth station namely a press E for vibratory compaction under vacuum, where the mixture 30 comprised between the two rubber sheets 20 and 32 is submitted to a compressive force and to a vibratory action under vacuum conditions;
- 25 (7) a seventh catalysis station F, where the catalysis reaction giving the finished product takes place.

In particular, the press E for the vibratory compaction comprises an adequately resistant supporting face and a vertically driven pressing and
30 vibrating hammer which are housed in a chamber from which the air is sucked in order to create the vacuum conditions required for the process to be carried out.

The Process according to the present invention comprises a step for the preparation of a mixture 26 which essentially consists of:

- 5 a) inorganic materials in a granular or powder form, with the optional addition of a filamentous inorganic material;
- b) binding materials;
- 10 c) accelerating, retarding and catalyst agents;
- d) additives intended to perform specific functions such as, for instance, adhesion promoting agents, fluidizing agents, anti-blistering agents, plasticizing and flexibilizing agents;
- 15 e) colouring substances in the form of liquids, powder, paste, granules and/or liquids of an inorganic and/or organic nature.

The material referred above as item a) is of a stony and/or calcareous
20 and/or siliceous type, such as quartzes or quartzites, granites and the like, coloured or non-coloured glass, even treated as a mirror, ceramic materials of all kinds, metals, shells, mothers-of-pearl, minerals of various kind.

25 The binding materials referred above as item b) are structural resins, such as polyester resins, epoxy resins, acrylic resins in the various formulations and combinations thereof.

The materials above referred as items c), d) and e) are of the types
30 normally used in the manufacturing processes of parts made of resins and agglomerate products in general.

The sequence according to which the various components are added to the mixture belongs to the common practice.

According to the present invention, the mixture 26, instead of being poured onto and spread over a paper sheet or a heat-resistant rubber tray board 20, as in the traditional techniques, is on the contrary poured onto and spread over a foil of thermoplastic material 50 (see Figure 5), such as polystyrene, which, under hot conditions, is sensitive to the action of the solvents which are present in the resin used as a binder in the mixture 26, in order to make easier the adhesion of the foil 50 to the same mixture.

As illustrated in Figure 2, a composite product 60 is then obtained which consists of a layer of compacted mixture 62 which is coupled to the foil 50 and has a size corresponding to the desired final composite product 60 (e.g. 310x135 cm).

From Figure 2 it can be noticed that the foil 50 has, on the side thereof facing the layer of mixture 62, a plurality of internally hollow protrusions or bosses 52 which are closed at their end 52a facing the mixture and open at the other end thereof. These protrusions or bosses 52 of the thermoplastic foil 50 are cylindrical in their shape (as illustrated in Figure 5): alternatively, instead of being cylindrical in their shape, they may have any different shape, with cross-sections (parallel to the plane of the foil 50) that may for example be elliptic, polygonal, star-shaped and so on.

25

The protrusions 52 penetrate the body of the agglomerate slab 62, thereby practically becoming an integral part of the same which they adhere to, in the same way as to said agglomerate slab eventually comes to adhere also the whole surface of the thermoplastic foil 50, which during the compaction phase is able to slightly roughen owing to the vibration of the granules constituting the mixture and, during softening in the next high-temperature catalysis phase, intimately links up with the

agglomerate slab 62 that undergoes shrinking while hardening. Such a softening allows the slab to shrink during the catalysis, without putting any restraint on it.

5 During the compaction phase of the agglomerate slab 62, the closed ends of the protrusions 52 can be subject to slight deformations, such as those shown schematically in Figure 4 in an exaggerated form for a better comprehension, thereby forming small undercuts which then constitute efficient points of anchorage to the laying plane in the case of thin tiles for
10 floorings (e.g. 5 mm).

For specific purposes, e. g. for further reducing the thickness of the final products and/or for several reasons, even application-related, the thermoplastic foil, instead of being provided with said protrusions, might
15 come without protrusions: the surfaces thereof might be smooth or corrugated, wrinkled, knurled or finished in any other way. The foil could also feature through holes, recesses and/or grooves or even undercuts.

Figure 6 illustrates the case of a composite product 64 comprising a
20 slab 62 with a thermoplastic foil 68 coupled thereto that is smooth externally and has a number of grooves or recesses 66 on the side thereof facing the mixture or slab 62, while Figure 7 shows a composite product 70 comprising a slab 62 coupled to a thermoplastic foil 74 having holes 72 which are penetrated by the compacted mixture of the slab 62.

25

One of the advantages of the composite product according to the present invention lies in the possibility of taking full advantage of the considerable physical-mechanical properties in terms of unit flexural-tensile and compressive strength of the traditional agglomerate slabs,
30 while however increasing the impact strength in the new composite structure, formed by the agglomerate slab 62 coupled to the thermoplastic foil 50, thereby making it possible for the product to be used also in large-

sized manufactured parts, notwithstanding its being very thin.

The impact strength of the new product can be further enhanced by adding filamentous aggregates, e. g. inorganic fibres like glass and/or
5 basalt fibres and the like, to the mixture 26 during the mixture phase.

It has been experimentally found that the addition of 7% glass-fibres to a mixture composed of 15% of unsaturated orthophthalic polyester resin of medium rigidity and 78% siliceous inorganic materials in granular or
10 powder form with a grain size of max. 1.2 mm has been effective in boosting by as much as approx. 3.5 times the impact strength of the composite product according to the present invention as compared with a corresponding conventional agglomerate slab.

15 In a variant of the present invention, the glass-fibres are used in the form of a gauze formed by bundles of glass filaments having an overall diameter of approx. 0.3 to 0.5 mm where meshes have a side size of approx. 10 mm, the said wire gauze being preferably laid upon the protrusions of the thermoplastic foil, so that it eventually is embedded in
20 the layer of mixture poured over the same gauze and ultimately adheres to the same protrusions, thereby forming a stable and firm link.

As an alternative approach, the fibreglass gauze can be embedded in the thickness of the mixture, which in the event is poured in two
25 subsequent steps so as to enable the gauze to be positioned exactly as desired within the thickness of the mixture and consequently of the resulting slab.

This result, due to the above mentioned fibre addition, may be of
30 particular interest when the usage of the composite product involves some kind of impact stress acting on the exposed surface of the thermoplastic foil and the need arises for an agglomerate layer of a greater strength.

The addition of such fibres is only provided for in view of special applications, since it is actually superfluous in normal applications, considering the fact that the impact strength measured on the surface of the agglomerate layer constituting the coupled agglomerate/thermoplastic foil composite product amounts to approx. 10 times the one typically measured on a traditional agglomerate without any foil coupled thereto.

Tests as follows were carried out on specimens having a plane size of 200 x 200 mm and a thickness of 7 mm, according to UNI 10442 standards:

- a) the novel composite product, i.e. with thermoplastic foil coupled thereto (without fibres) :
 - 15 - impact strength on the exposed face of the agglomerate: 3.9J
 - impact strength on the exposed face of the foil: 1.5J;
- b) the novel composite product, i.e. with thermoplastic foil coupled thereto and with the addition of glass fibres (7%):
 - 20 - impact strength on the exposed face of the agglomerate: 6.4J
 - impact strength on the exposed face of the foil: 3.7J;
- c) a conventional agglomerate slab (without any foil coupled thereto) with the addition of 7% glass fibres:
 - 25 - impact strength: 3.9J.

By way of reference it should be noticed that a traditional agglomerate slab with the same dimensions, the same thickness and the same composition, but without any addition of glass fibers and without any reinforcing thermoplastic foil, has an impact strength of 1.47 J.

The new composite product obtained under the addition of fibres

maintains, and slightly improves, the excellent flexural-tensile strength properties of the conventional agglomerate (product) slab.

Figure 8 illustrates a composite end product 80 obtained according to a first variant of the invention, in which during the manufacturing process there is first of all poured and distributed, i.e. spread, a first layer of mixture, on which the thermoplastic foil 50 is then laid, and finally there is poured and spread a second layer of mixture. The composite end product 80 so manufactured consists of a thermoplastic foil 50 sandwiched between two agglomerate slabs 62a, 62b.

Figure 9 illustrates a composite end product 90 obtained according to a second variant of the present invention, in which during the manufacturing process the mixture is poured on to a double foil 50a, 50b obtained by approaching the protrusions of the two foils 50 to each other in a mutually opposed manner, and joining said protrusions with each other, e.g. by means of hot welding spots at their closed end portions 52a

This is therefore an embodiment which is practically similar to the one shown in Figures 2 and 3, with a variant consisting in doubling the thermoplastic foil reinforcement. Such a solution may be used in view of obtaining greatly enhanced mechanical properties.

It should be noticed that the two elements being coupled to form the composite end product are characterized by two different coefficients of linear thermal expansion: for instance, the polystyrene foil has a coefficient of $70 \text{ to } 80 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, whereas the agglomerate slab has a coefficient of $25 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. This might cause the composite product to undergo some bending effect under changing temperature conditions. This risk is overcome by selecting the most appropriate thickness for each one of said two elements in order to nullify the above cited effect.

For example, if an agglomerate slab with a thickness of 7 mm is coupled to a polystyrene foil having a thickness of 0.6 mm, the different linear expansion of the two elements does not bring about any practical effect for the flatness of the system exposed to ambient conditions where
5 the temperature is subject to variations within a range from +7°C to +40°C, such as the ones usually prevailing in dwelling rooms.

Correspondingly, the same applies to an agglomerate slab with a thickness of 13 mm, when it is coupled to a polystyrene foil with a
10 thickness of 1.2 mm.

In case of products intended for outdoor installation, where temperature variations may take place within a range from -5°C to +60°C, a proper selection of the thickness of the products is made and, therefore,
15 of the two main component parts thereof, in order to nullify the effects of the higher temperature changes.

Such a behaviour is a constant one in composite products (slabs) up to a size of 120x240 cm.

20

In case of even bigger sizes, modest deviations may occur, which however, thanks to the elasticity of the composite product, can be most easily corrected by the simple manual pressure exerted by an installer.

25 On the other hand, when installed, the composite product will not show any deviations from flatness.

It will of course be appreciated that any conceptually or functionally similar variant that may be further developed by those skilled in the art
30 does not depart from the scope of the appended claims.

So, for example, the material which the thermoplastic foil 50 may be

made of, is not limited to polystyrene, but can on the contrary be any other thermoplastic material that is capable of firmly adhering to the structural resin that can be found on the surface of the agglomerate slab.

5

* * * * *

CLAIMS

1. Composite product comprising a slab of an agglomerate formed by inorganic materials in granular and/or powder form, and possibly also by filamentous materials, which are bound with the use of a structural resin, **characterized in that** to said slab of agglomerate material (62) there is associated at least one foil of thermoplastic material (50).
2. Composite product according to claim 1, **characterized in that** said at least one foil (50) is coupled to said agglomerate slab (62) externally.
3. Composite product according to claim 1, **characterized in that** said at least one foil (50) is embedded within said agglomerate slab (70).
4. Composite product according to claim 2 or 3, **characterized in that** said foil (50) has smooth and/or embossed and/or corrugated and/or grooved and/or perforated surfaces.
5. Composite product according to any of the preceding claims 1 to 4, **characterized in that** said at least one foil (50) is provided with protrusions (52) adapted to be embedded in the mixture which said slab (62) is made of.
6. Composite product according to claim 5, **characterized in that** said protrusions (52) are internally hollow, closed at their end facing the mixture and open at the opposite end.
7. Composite product according to claim 6, **characterized in that** said protrusions (52) have a curvilinear shape in their cross-section parallel to the plane of the foil (50).
8. Composite product according to claim 7, **characterized in that** said

protrusions (52) are circular in their cross-section, so that the same protrusions have a cylindrical shape.

9. Composite product according to claim 7, **characterized in that** said
5 protrusions (52) are elliptical in their cross-section.

10. Composite product according to claim 6, **characterized in that**
said protrusions (52) have a polygonal shape in their cross-section parallel
to the plane of the foil (50).

10

11. Composite product according to claim 1, **characterized in that** it
is provided with a double thermoplastic foil composed by two foils (50a,
50b), each one of which is provided with protrusions that are closed at the
upper end portion (52a), internally hollow and open at the opposite end
15 portions, said foils facing each other in a mutually opposing manner and
being joined with each other at the closed end portions (52a) of the
protrusions (52).

12. Composite product according to any of the preceding claims 1 to
20 11, **characterized in that** it contains fibres in the agglomerate slab (62).

13. Composite product according to claim 12, **characterized in that**
said fibres are in the form of a wire gauze.

25 14. Composite product according to claim 13, **characterized in that**
said fibre gauze is embedded in said agglomerate slab (62).

15. Composite product according to claim 1, **characterized in that**
said agglomerate slab contains decorative elements, such as pieces of
30 coloured glass, mirror glass, ground marble and granite, shells, metal
fragments, ceramic materials and the like.

16. Process for manufacturing composite products comprising agglomerate slabs constituted by inorganic materials in granular and/or powder form which are bound with each other by means of an organic binder, in which said process comprises the steps of preparing a mixture
5 (26) permeable to air, capable of being de-aerated and compacted; pouring said mixture (26) onto a support (20); submitting the mixture (26) to vibratory compaction, in which said mixture is pressed and vibrated in an ambient at a lower pressure than the atmospheric one; heating the compacted mixture up to the catalysis temperature of the organic binder
10 so as to allow the mixture (26) to harden, **characterized in that**, prior to the pressing step, to the mixture (26) there is added at least one foil (50) of thermoplastic material, which at the end of the hardening step of the mixture turns out to be firmly coupled to the agglomerate slab (62).

15 17. Process according to claim 16, **characterized in that** said at least one thermoplastic foil (50) is added to the mixture (26) before the step where said mixture (26) is poured onto said support.

18. Process according to claim 16, **characterized in that** said at least
20 one thermoplastic foil (50) is added after said mixture pouring step.

19. Process according to claim 16, **characterized in that** said thermoplastic foil (50) is added to the mixture (26) after a first layer of mixture (26) has been poured onto said support (20), and is then covered
25 with a second layer of mixture (26).

20. Process according to claim 16 or 17, **characterized in that** said at least one foil (50) is provided with protrusions (52) intended to be embedded in the agglomerate slab (62).

30

21. Process according to claim 20, **characterized in that** said protrusions (52) are internally hollow, closed at their end facing the

mixture and open at the opposite end.

22. Process according to claim 16 or 17, **characterized in that** said mixture (26) is poured on and spread over a double thermoplastic foil composed by two foils (50a, 50b), each one of which is provided with protrusions that are closed at the upper end portion (52a), internally hollow and open at the opposite end portion, in which said foils are facing each other in a mutually opposing manner and are joined with each other at the closed end portions (52a) of the protrusions (52).

10

23. Process according to any of the preceding claims 16 to 22, **characterized in that** said foil (50) has smooth and/or embossed and/or corrugated and/or grooved and/or perforated surfaces.

15 24. Process according to any of the preceding claims 16 to 23, **characterized in that** material in fibre form is introduced in said mixture (26).

25 25. Process according to claim 24, **characterized in that** said material is constituted by mineral fibres.

26. Process according to claim 25, **characterized in that** said material is glass fiber.

25 27. Process according to claim 26, **characterized in that** said glass fiber material is in an amount ranging from 3% and 8% as referred to the volume of the mixture.

28. Process according to claim 26, **characterized in that** said glass fiber material is in the form of a wire gauze.

29. Process according to claim 16, **characterized in that** said organic

binder is a structural resin.

30. Process according to claim 29, **characterized in that** said structural resin is selected among polyester, epoxy and acrylic resins.

5

31. Process according to any of the preceding claims 16 to 30, **characterized in that** said inorganic materials comprise decorative elements including pieces of coloured glass, mirror glass, ground marble and granite, shells, metal fragments and ceramic materials.

10

32. Process according to any of the preceding claims 16 to 31, **characterized in that** the mixture is poured onto a sheet or tray (20) made of an elastic material, and the mixture (26) is then covered with a cover (32) which is also made of an elastic material.

15

33. Process according to any of the preceding claims 16 to 31, **characterized in that** the mixture is poured onto a first sheet of paper, which may even be treated, and the mixture (26) is then covered with a second sheet of paper.

20

34. Process according to any of the preceding claims 16 to 33, **characterized in that** the hardening step of the mixture is carried out at temperatures that are higher than the softening temperature of the thermoplastic foil (50).

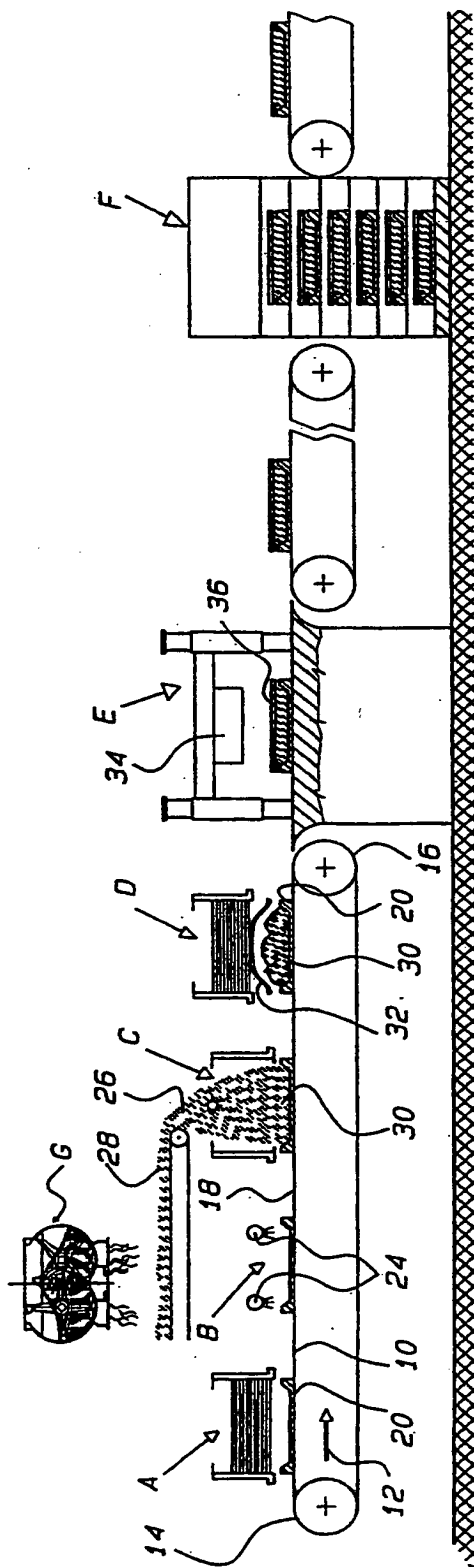


Fig. 1

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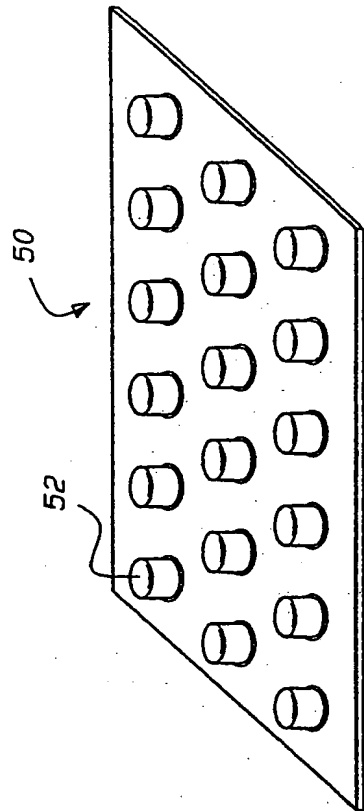


Fig. 5

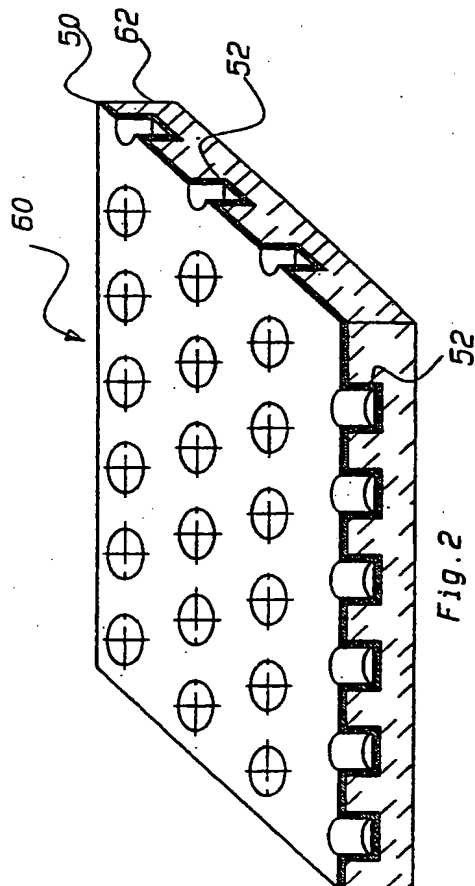


Fig. 2

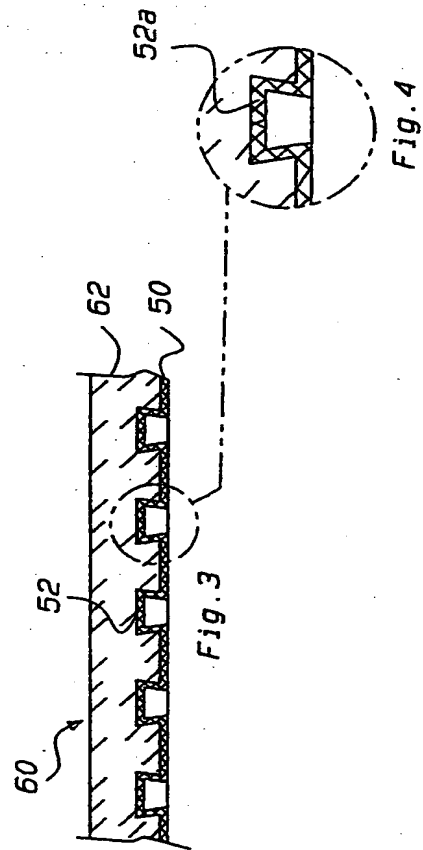


Fig. 4

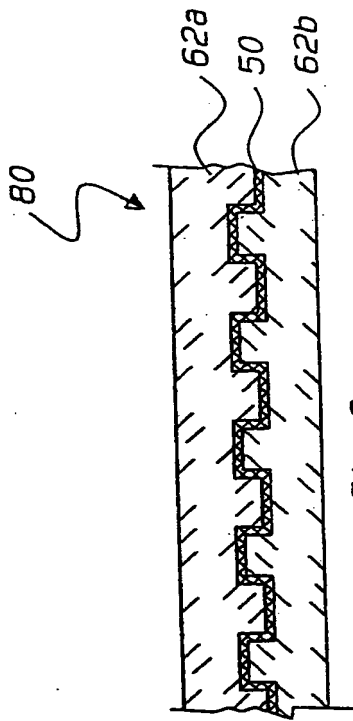


Fig. 8

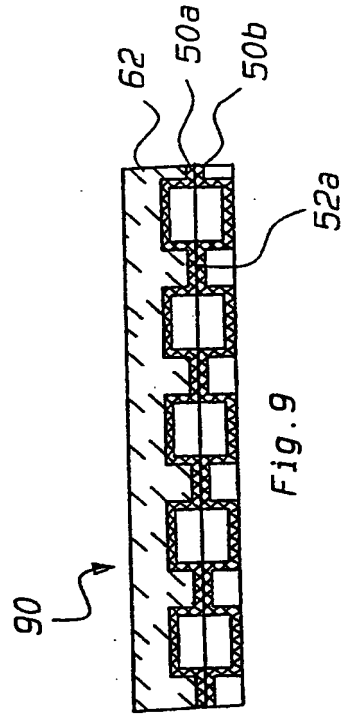


Fig. 9

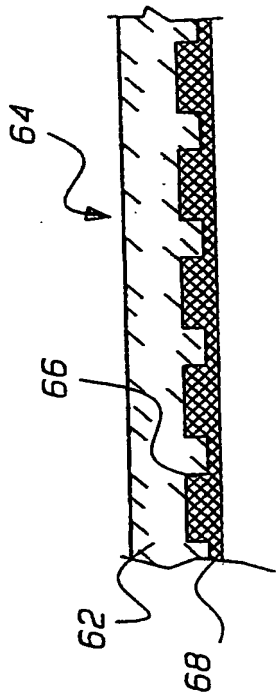


Fig. 6

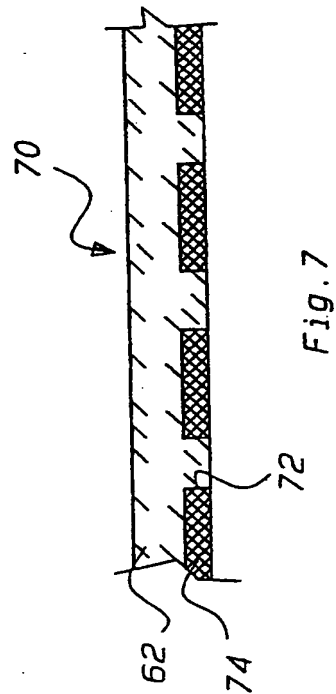


Fig. 7

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B32B 27/00, 3/30, B29C 37/00

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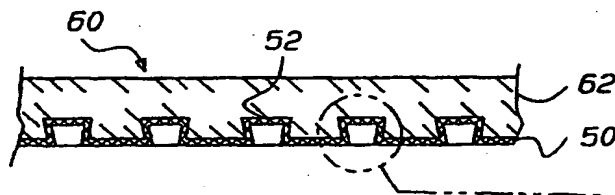
(26) Publication Language: English

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(72) Inventor: TONCELLI, Marcello [IT/IT]; Via Papa Giovanni XXIII, 2, I-36061 Bassano del Grappa (IT).

(54) Title: IMPROVED SLAB OF RESIN-BOUND AGGLOMERATE MATERIALS AND RELATED MANUFACTURING PROCESS



(57) Abstract: Composite product formed by a slab consisting of an agglomerate of granular and filamentous inorganic materials bound with the use of structural resins which is coupled to a foil of thermoplastic material, and manufactured with a process comprising the steps of: a) preparation of a mixture capable of

releasing air, i.e. adapted to be de-aerated; b) association to the mixture of a foil of thermoplastic material having hollow protrusions that are closed at their end facing the mixture; c) transfer of the mixture, enclosed between a sheet or tray and a cover, to a press where it is de-aerated and pressed under vacuum in order to obtain the manufactured product in a raw state; d) application of heat to said raw product, while it still is enclosed between the above mentioned sheet or tray and cover, through a pair of heating planes in order to harden the binding resin.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/12424

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B29C70/78 B32B27/00 B32B3/30 B29C37/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29C B32B E04C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 759 092 A (E. BENTZ) 10 October 1956 (1956-10-10) the whole document	1,2, 12-17, 23,24, 26-31
X	FR 1 465 637 A (C. LAINE') 29 March 1967 (1967-03-29) the whole document	1,2,4, 12,15, 16,23-31
X	EP 0 399 707 A (VEDRIL SPA) 28 November 1990 (1990-11-28) the whole document	1,2,4
A	US 5 759 658 A (R. M. PIEKOS) 2 June 1998 (1998-06-02) the whole document	1,16
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27 June 2001

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A	US 5 928 585 A (TONCELLI MARCELLO) 27 July 1999 (1999-07-27) cited in the application the whole document & IT 1 288 566 A (M. TONCELLI) 23 September 1998 (1998-09-23) -----	1,16,32
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 12, 31 October 1998 (1998-10-31) -& JP 10 180913 A (ASAHI GLASS ENG KK), 7 July 1998 (1998-07-07) abstract; figures 1,2 -----	1,5

INTERNATIONAL SEARCH REPORT

In relation on patent family members

International Application No

PCT/EP 00/12424

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 759092	A		NONE	
FR 1465637	A	29-03-1967	NONE	
EP 0399707	A	28-11-1990	IT 1229708 B AT 140183 T DE 69027715 D NO 175197 B	07-09-1991 15-07-1996 14-08-1996 06-06-1994
US 5759658	A	02-06-1998	NONE	
US 5928585	A	27-07-1999	IT TV960007 A CA 2196119 A EP 0786325 A TR 9700056 A	29-07-1997 30-07-1997 30-07-1997 21-08-1997
JP 10180913	A	07-07-1998	NONE	

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